

REMARKS

Applicant has amended his claims in order to further clarify the definition of various aspects of the present invention. Specifically, Applicant has canceled previously considered claims 1-19 without prejudice or disclaimer, and have added new claims 20-32 to the application. All of these newly added claims are directed to a method of manufacturing a semiconductor integrated circuit device, with claim 20 being the sole newly added independent claim.

Independent claim 20 recites that the method includes steps of providing a silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide, and cleaning the surface of the silicon wafer using a processing solution which contains hydrogen peroxide, hydricid fluoride salt and water, concentration of the salt in the processing solution being in a range of about 0.1-3 mol/l; removing the insulating film after cleaning the surface of the silicon wafer, to expose the surface of the wafer; and subjecting the silicon wafer to a heat-treatment after removal of the insulating film, to form a gate oxide film over the silicon wafer. Note, for example, the third full paragraph on page 7 of Applicant's specification. Claims 21 and 22, each dependent on claim 20, further define the hydricid fluoride salt; and claims 23 and 24, each also dependent on claim 20, respectively recites that the processing solution includes HF and HF₂ as etching seeds of silicon oxide, and recites that the processing solution further includes a surfactant. Claims 25 and 26, each dependent on claim 20,

respectively recites that the method further includes a step of cleaning a surface of the silicon wafer during ultrasonic vibration of the processing solution; and recites that the processing solution has a pH in a range of 6-11. Claims 27 and 28, each dependent on claim 20, respectively recites that the processing solution has a temperature as low as 40°C, during the cleaning; and recites that the insulating film is removed by dipping in a mixed solution of hydrofluoric acid and water. Claim 29, dependent on claim 20, recites that after the insulating film is removed and prior to subjecting the silicon wafer to the heat-treatment to form the gate oxide film, the silicon wafer is dried; and claim 30, dependent on claim 29, recites that after this drying the silicon wafer is immediately transferred to a chamber for subjecting the silicon wafer to the heat-treatment for forming the gate oxide film. Claims 31 and 32, dependent respectively on claims 30 and 20, each recites the further step of performing another heat-treatment, after forming the gate oxide film, in an atmosphere of NO or N₂O, to segregate nitrogen at the interface between the gate oxide film and the silicon wafer.

In connection with the newly added claims, note pages 6, 7 and 13-19 of Applicant's specification, particularly together with Figs. 4-8, 10 and 11 of Applicant's disclosure.

The objection to claim 2 as set forth in Item 1 on page 2 of the Office Action mailed December 7, 2001, is noted. This objection is moot in light of canceling of claim 2.

The rejection of claims 5 and 12 under the second paragraph of 35 USC 112, as set forth in Item 3 on page 2 of the Office Action mailed December 7, 2001, is noted. This rejection is moot in light of present canceling of claims 5 and 12.

In addition, attention is respectfully directed to newly added claim 27. It is respectfully submitted that claim 27 clearly satisfies requirements of the second paragraph of 35 USC 112, with respect to temperature of the processing solution during the cleaning.

Applicant respectfully submits that all of the claims now presented for consideration by the Examiner patentably distinguish over the teachings of the references as applied by the Examiner in rejecting claims in the Office Action mailed December 7, 2001, that is, the teachings of the U.S. patents to Szwejkowski, et al., No. 5,296,093, to Ohmi, et al., No. 5,990,060, and to Yoon, et al., No. 6,117,350, under the provisions of 35 USC 102 and 35 USC 103.

It is respectfully submitted that these references as applied by the Examiner would have neither taught nor would have suggested such a method of manufacturing a semiconductor integrated circuit device as in the present claims, including, inter alia, wherein the surface of a semiconductor wafer, covered with an insulating film whose main surface is mainly formed of silicon oxide, is cleaned using a processing solution which contains hydrogen peroxide, hydric acid fluoride salt and water, with concentration of this salt being in a range of about

0.1-3 mol/l; and, thereafter, removing the insulating film to expose the surface of the silicon wafer, and subjecting the silicon wafer after removal of the insulating film to a heat-treatment to form a gate oxide film over the silicon wafer. See claim 20.

That is, as set forth in claim 20, and as will be further discussed infra, it is respectfully submitted that these references do not disclose, nor would have suggested, wherein the surface of a semiconductor wafer covered with an insulating film whose main surface is mainly formed of silicon oxide is cleaned using the recited processing solution, and thereafter are performed steps of removing the insulating film and then forming a gate oxide film over the silicon wafer.

In addition, it is respectfully submitted that the teachings of the applied references would have neither disclosed nor would have suggested the other aspects of the present invention as in the remaining, dependent claims, wherein the specified cleaning step is performed prior to forming the gate oxide film, and including (but not limited to) wherein the hydracid fluoride salt is ammonium fluoride or tetraalkyl ammonium fluoride (note claims 21 and 22, respectively); or wherein the processing solution includes HF and HF_2^- as etching seeds of silicon oxide (note claim 23); or wherein the pH of the processing solution is in a range of 6-11 (note claim 26); or wherein a step of cleaning during ultrasonic vibration of the processing solution is performed (see claim 25); or temperature

of the processing solution during the cleaning as in claim 27; or wherein the insulating film is removed by dipping in a mixed solution of hydrofluoric acid and water (see claim 28); or the additional drying step, after the insulating film is removed and prior to forming the gate oxide film (note claim 29), with the silicon wafer being immediately transferred to a chamber for forming the gate oxide film, after drying (note claim 30); or the additional heat-treatment in an atmosphere of NO or N₂O, segregating nitrogen at the interface between the gate oxide film and the silicon wafer (see claims 31 and 32).

The present invention is directed to a method of manufacturing a semiconductor integrated circuit device, particularly advantageously applied to a cleaning process for a silicon wafer in cleaning the wafer prior to forming a gate oxide film of the device.

In manufacturing a large scale integrated circuit device using a wafer made of mono-crystalline silicon, a so-called RCA wafer cleaning technique has been used, as described in the paragraph bridging pages 1 and 2 of Applicant's specification.

However, there is a desire to improve the RCA cleaning technique, and various attempts for improvement thereof have been made, as described on pages 2-4 of Applicant's specification. However, these proposed techniques have been insufficient, particularly for the process of forming a gate of a MOSFET which

requires a thin gate oxide film of high quality. See the second full paragraph on page 4 of Applicants' specification.

Against this background, Applicant provides a method having especially advantageous effects for cleaning a semiconductor wafer, in processing for forming a gate oxide film of a semiconductor integrated circuit device.

Applicant has found that by utilizing a processing solution containing hydrogen peroxide, hydrazine fluoride salt and water, for cleaning the surface of the silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide; and with this insulating film thereafter being removed to expose the surface of the silicon wafer and the silicon wafer then being subjected to a heat treatment to form the gate oxide film, the cleaning can be performed at relatively low temperatures and wherein the silicon oxide film is cleaned and etched without etching the silicon substrate, so that contamination of the substrate can be avoided. Moreover, through use of the processing solution of the present invention, in processing steps leading up to and including the formation of the gate oxide film, the cleaning can be accomplished in a short time and at a low temperature, without deteriorating flatness of the wafer surface. Note, for example, the first full paragraph on page 6 of Applicant's specification.

Furthermore, through use of the further, oxy-nitrifying processing performed after forming the gate oxide film, nitrogen is segregated at the

interface between the gate oxide film and the wafer, and this segregation of nitrogen at the interface moderates distortion at the interface inducing occurrence of hot carriers, thereby improving reliability of the gate oxide film. Note the paragraph bridging pages 18 and 19 of Applicant's specification.

Szwejkowski, et al. discloses a process for removing residues remaining after etching a polysilicon layer on an integrated circuit structure. The process removes sidewall residues remaining from anisotropic etching of a polysilicon layer, which is formed over a step and masked with a photoresist, these residues including residues of a polymerized material containing both silicon and oxide remaining adjacent the sidewalls of the masked portions of polysilicon after the etch. The process disclosed in this patent includes treating the integrated circuit substrate, after the anisotropic etching step, and preferably after stripping of the photoresist mask, with an aqueous solution of ammonium-containing base/peroxide to remove the polymeric residues of silicon and oxide-containing material, formed on the sidewall of the polysilicon line, without undercutting the remaining polysilicon. Note particularly column 2, lines 31-46. See also column 3, lines 37-40. This patent discloses that the treatment with the aqueous ammonium-containing base/peroxide solution will remove the undesired residues with minimum damage to the exposed oxide on substrate 2, for example, gate oxide 4 (note Fig. 4).

It is respectfully submitted that Szwejkowski, et al. discloses processing utilizing the aqueous solution, after formation of the gate oxide, as is clear from column 3, lines 20-31 of this patent. It is respectfully submitted that this patent would have neither disclosed nor would have suggested, and in fact would have taught away from, the presently claimed method, including cleaning, with the specified solution, the silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide, and thereafter removing the insulating film to expose the surface to the silicon wafer and then subjecting the silicon wafer to a heat-treatment to form the gate oxide film, as in claim 20, or the additional aspects of the present invention as in the other presently pending claims.

The contentions by the Examiner on page 4 of the Office Action mailed December 7, 2001, with respect to claims 15, 16, 18 and 19, are noted. However, as is clear from the description in connection with Fig. 4 of Szwejkowski, et al., as discussed previously, in Szwejkowski, et al. the cleaning is performed after formation of the gate oxide, which would have taught away from the present claimed subject matter.

Yoon, et al. discloses solutions used in etching semiconductor devices, and methods of using such solutions for etching. The methods for etching include contacting semiconductor devices with solutions including ammonium fluoride, hydrofluoric acid, hydrogen peroxide and water to etch the

semiconductor devices, the semiconductor devices being etched including a substrate and an oxide layer present thereon. See column 2, lines 36-42 of Yoon, et al. This patent further discloses that the solutions can include surfactants to improve the wetting characteristics of the solutions on the devices by lowering the interfacial energies of the solutions. See column 3, lines 11-13. This patent discloses the method is particularly effective for removing a layer of material, typically silicon, which has been damaged by ions of high energy used during etching, for example, under a trench formed by the etching, the damaged layer being contacted by the solution so as to become etched. See column 3 lines 53-59.

It is respectfully submitted that Yoon, et al. would have neither taught nor would have suggested the presently claimed process, including processing steps (including cleaning) leading up to and including a heat treatment to form a gate oxide film, as in claim 20, much less the other aspects of the present invention as in the remaining claims and as discussed previously.

Ohmi, et al. discloses a cleaning method and a cleaning device which can remove foreign materials deposited on a substrate after removal of photoresist by plasma processing. See column 1, lines 6-10. This patent discloses that foreign materials can be removed under room temperature, by using a cleaning liquid which is a basic and water-soluble fluoride and an oxidizing agent, mixed in pure water. Note column 2, lines 20-29. See also column 2, lines 37-39 and 48-

51; column 3, lines 42-47; and column 4, lines 45-50. This patent further discloses that by irradiating ultrasonic waves to the cleaning liquid or pure water, it is possible to improve the cleaning effect. Note the paragraph bridging columns 3 and 4 of this patent. This patent further discloses that the cleaning liquid can be applied not only to removal of photoresist, but also to removal of various types of high polymer organic coating films such as paint or adhesive, films of machine oil, as well as removal of surface surfactant or dye or the like. See column 8, lines 24-34. Note also the paragraph bridging columns 2 and 3; and column 5, lines 7-10, of Ohmi, et al.

It is emphasized that Ohmi, et al. is primarily concerned with a cleaning liquid and cleaning method removing organic materials, particularly removal of photoresist. It is respectfully submitted that this patent is primarily concerned with removal of photoresist in connection with ion injection or reactive ion etching processes. It is respectfully submitted that this patent does not disclose, nor would have suggested, the presently claimed method, including performance of the recited cleaning using the specified processing solution, prior to and leading up to and including forming the gate oxide film, and advantages achieved.

Moreover, it is respectfully submitted that these applied references do not disclose, nor would have suggested, in processes including the cleaning and

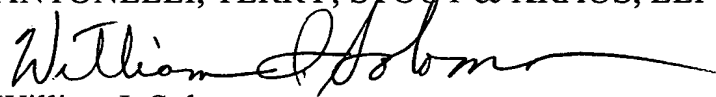
leading up to and including formation of the gate oxide, concentration of the hydricid fluoride salt in the processing solution, as in claim 20.

In view of the foregoing comments and amendments to the claims, reconsideration and allowance of all claims remaining in the application are respectfully requested.

To the extent necessary, Applicants petition for an extension of time under 37 CFR 1.136. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to the Deposit Account No. 01-2135 (Case No. 843.37558VX1) and please credit any excess fees to such Deposit Account.

Respectfully submitted,

ANTONELLI, TERRY, STOUT & KRAUS, LLP

A handwritten signature in black ink, appearing to read "William I. Solomon", written over the printed name.

William I. Solomon
Registration No. 28,565

1300 North Seventeenth Street
Suite 1800
Arlington, VA 22209
Tel.: 703-312-6600
Fax.: 703-312-6666

WIS/slk